Thermal analysis of new glycopolymers derived from monosaccharides

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Abstract A novel monomer carrying carbohydrate moiety was prepared by simple reaction of methacrylic acid with 3-O-(2',3'-epoxy-propyl)-1,2:5,6-di-O-isopropylidene-a-D-glucofuranose. Another D-glucose oligomer was synthesized by the polycondensation of a dicarboxylic acid including the carbohydrate residue into the main polymeric chain, 3-O-benzyl-5,6-(bis-O-(acryloyloxy))-1,2-di-O-isopropylidene- α -D-glucofuranose, with propane-1,3-diol using ptoluenesulfonic acid as catalyst. These products were copolymerized with styrene and 2-hydroxypropyl methacrylate, respectively, at different mass ratios, using benzoyl peroxide as initiator. Differential scanning calorimetry was performed in order to study the copolymerization process of the monomer and oligomer into the chosen co-monomers, respectively, and the activation energy of this process was evaluated using Kissinger-Akahira-Sunose (KAS) method. The storage and loss modulus of the obtained glycopolymers were evaluated using dynamic mechanical analysis. The thermal stability of the obtained products was studied via thermogravimetry.

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Introduction

Polymers are one of the most widely used materials in our every day life, intensively applied in medicine, as well in the food and the cosmetics industries. The global consumption of plastic is more than 200 million tons a year. Due to growing environmental concerns, the field of biodegradable polymers has been gaining widespread attention [1]. New polymeric materials derived from renewable sources, like carbohydrates draw attention to public eye, especially because of their advantages like high biocompatibility and biodegradability. Since the petroleum resources are limited and petroleum-based polymers have caused many environmental problems, these environmentally friendly materials can provide alternatives to conventional non-biodegradable plastics [2–5].

Inspired by the chemical and physical structures of natural polysaccharides, glycopolymers have been synthesized and widely studied in the past 35 years [6, 7]. Synthetic carbo-hydrate-containing macromolecules or glycopolymers have attracted increasing attention in various fields of science with particular interest to the biological sciences due to their recognition properties [8–10]. Advances in synthetic chemistry allow for the preparation of well defined and multi-functional glycopolymers in a relatively facile manner [11]. There is a great interest in the polymer-supported synthesis of oligosaccharides and glycoconjugates with potential applications in the biomedical, biological and innovative packing films areas [12–14]. Recent research in the field of polymers has focused on getting the new methods that allow control over the molecular structure and molecular

mass. The development of synthetic polymers using monomers from renewable resources provides a new opportunity to obtain biodegradable polymers [15-17].

Thermal analysis is an integral part of research and development of new materials. The physicochemical processes that occur during the thermolysis of any given material control their performance. It also provides a relative measure of their thermal stability. Thus investigation of thermal processes kinetics of new materials is important for their performance prediction and safety evaluation [18].

Using of the low molecular mass carbohydrates (glucose) as renewable resources to obtain glycomonomers and their corresponding glycopolymers has attracted our interest. From this point of view, the aim of our experiments was to obtain environmentally compatible polymers from monosaccharides. This paper presents the thermal properties of new materials derived from monosaccharides, namely glycopolymers. The glycopolymers were obtained by using a D-glucose-based glycomonomer, 3-O-(2'-hydroxy-3'-methacryloyloxypropyl)-1,2:5,6-di-O-isopropylidene-a-D-glucofuranose (4) and of a new D-glucose-based oligomer (8), synthesized by the polycondensation of a dicarboxylic acid including the carbohydrate residue into the main polymeric chain, namely 3-O-benzyl-5,6-(bis-O-(acryloyloxy))-1,2-di-O-isopropylidene- α -D-glucofuranose, with propane-1, 3-diol using *p*-toluenesulfonic acid as catalyst. The copolymerization properties of the new monomer and the new oligomer with styrene (S) and 2-hydroxypropyl methacrylate (HPMA), respectively, were studied via differential scanning calorimetry (DSC). The thermal stability of the copolymerized products, namely the glycopolymers, was studied by thermogravimetry; thermogravimetric analysis (TG) is a method which can be used to measure the mass change, thermal decomposition and thermal stability of polymer materials [19]. The mechanical properties of the glycopolymers were evaluated using dynamic mechanical analysis (DMA).

Experimental

Materials and methods

All reagents were used as purchased. The syntheses were monitored using thin-layer chromatography performed on silica gel plates, Merck silica gel 60 F_{254} aluminum sheets, using different eluant mixtures. The FTIR-ATR spectra were recorded using a Jasco FT/IR-410 spectrometer, at room temperature, using the ATR device. The samples were analyzed over the range 3,800–600 cm⁻¹, operating a 4 cm⁻¹ resolution.

The copolymerization process of D-glucose monomer and oligomer with styrene and HPMA, respectively, was studied using DSC. The DSC diagrams were recorded on a Netzsch 204 DSC device in inert atmosphere, using the heating range of 20–200 °C and variable heating rates (2.5, 5, 7.5, 10, 20 °C min⁻¹), operating Proteus Analysis software. The samples were placed in liquid form, an average of 4.0 ± 0.1 mg in closed aluminum crucibles (average mass 39 ± 0.2 mg) and analyzed according to the established heating program.

The mechanical properties of glycopolymers were studied using DMA on a Netzsch DMA 242 C, at temperature ranging between -100 and 100 °C and strain frequencies 1, 2, 5, 10 and 20 Hz. The samples were placed in form of cylinders (4.6 mm diameter and average height of 5.0 ± 0.5 mm) and the heating rate was 2 °C min⁻¹.

In order to determine the thermal stability of the obtained products TG analysis was carried out using a Netzsch TG 209, operating a resolution of 0.1 μ g, in nitrogen atmosphere. For the TG measurements, the start temperature was 20 °C, the end temperature was 500 °C, and the applied heating rate was 10 °C min⁻¹. The average sample mass was 4.0 \pm 0.15 mg in open alumina crucibles (average mass 190 \pm 1.0 mg).

Monomer and oligomer synthesis and their copolymerization

Monomer and oligomer were obtained by the procedure describe previously according to Figs. 1 and 2 [20, 21]. For their copolymerization, we have used the following procedure: the monomer and oligomer were dissolved in styrene and HPMA (mass ratio 1:1, 1:2, 1:3, 1:4), respectively, and then the initiator—benzoyl peroxide (BPO) is added (1 wt% from the mixture); the mixture is stirred until perfect homogeneity is achieved. This mixture was then placed into cylindric glass tubes. The temperature was increased gradually with 10 °C per hour until 110 °C.

Preparation of DSC sample

The monomer and oligomer were dissolved into a certain amount of styrene and HPMA, respectively, at different mass ratio, and then the initiator BPO is added (1 % from the mixture). The mixture is stirred vigorously until the peroxide is dissolved, then the mixture was analyzed using DSC (Table 1).

Results and discussions

The ATR-FTIR analysis

Figure 3 presents the FTIR spectra of the Gm_Sx glycopolymers. The IR spectra of the copolymers confirm their

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Fig. 2 Preparation of the D-glucose oligomer: (*v*) BnBr, NaH, DMF, MeOH; (*vi*) CH₃COOH, 80 %, 45 min, 70–75 °C; (*vii*) MAh, TEA, 20 h, 60 °C



Table 1 The samples prepared for DSC analysis

D-Glucose monomer (Gm)-derived glycopolymers sample	D-Glucose oligomer (Go)-derived glycopolymers sample	Mass ratios D-Glucose oligomer:HPMA D-Glucose monomer:styrene
Gm_S1	Go_HPMA1	1:1
Gm_S2	Go_HPMA2	1:2
Gm_S3	Go_HPMA3	1:3
Gm_S4	Go_HPMA4	1:4

structure. The signals at about $3,000-3,100 \text{ cm}^{-1}$ express the C–H aromatic from the styrene skeleton, while the signals from $2,800-3,000 \text{ cm}^{-1}$ are specific to methylene and methyl groups from the glycopolymer skeleton. The C–O and C=O esteric bond are placed at about 1,180 and 1,700 cm⁻¹, respectively. The OH from the monomer structure appears at about 3,400 cm⁻¹. Similar spectra were obtained in the case of the D-glucose oligomer-based

glycopolymers, the IR spectra confirming the total copolymerization of the monomers into one another, by the absence of the C=C signal, from about $1,640 \text{ cm}^{-1}$.



Fig. 3 ATR-FTIR spectra of the copolymers (Gm_Sx)

The characterization of the copolymerization process using DSC

To assess the kinetics of the copolymerization process between glycomonomer and styrene and between the oligomer and HPMA in the presence of BPO, KAS isoconversional method was used. From the DSC diagrams (Figs. 4, 5) obtained, it can be observed that the copolymerization of the monomer with styrene occurs from about 100 to 140 °C, while the copolymerization of the oligomer with HPMA takes place from about 90 to 30 °C, concluding that the oligomer-derived glycopolymers can be obtained at lower temperatures [22]. This fact can be explained by the affinity the co-monomers have to one another during the copolymerization process, and considering the long chain of the oligomer which has 8 mer units



Fig. 4 DSC diagrams for the copolymerization of D-glucose monomer with styrene (mass ratio 1:2) at different heating rates



Fig. 5 DSC diagrams for the copolymerization of D-glucose oligomer with HPMA (mass ratio 1:3) at different heating rates

Table 2 Peak temperatures for the copolymerization process at 5 $^{\circ}\mathrm{C}\ \mathrm{min}^{-1}$

Sample	Peak temperature/°C	Sample	Peak temperature/°C
Gm_S1	110.5	Go_HPMA1	102.4
Gm_S2	126.4	Go_HPMA2	105.7
Gm_S3	127.2	Go_HPMA3	107.7
Gm_S4	127.6	Go_HPMA4	113.5

[21] connected and that allow the crosslinking with the HPMA monomer.

It can be observed that the peak temperature increases with the rise of the heating rates and along the increase of mass ratio. The copolymerization process occurs in one step for the mentioned co-monomers, in all cases discussed (mass ratios, heating rates, composition) and the copolymerization process for the D-glucose oligomer into HPMA occurs at lower temperatures than for D-glucose monomer into styrene (Table 2), subsequently that would lead to the same pattern for the activation energy of the copolymerization process. To evaluate the activation energies of the copolymerization process of the monomer and the oligomer, respectively, into the given monomers we have used an isoconversional method, Kissinger–Akahira–Sunose (KAS).

The Kissinger-Akahira-Sunose (KAS) method

All of the isoconversion methods require the determination of the temperature $T_{\alpha i}$ at which a fixed fraction α (conversion) of the total amount is transformed. In the KAS method, the relation between the temperature $T_{\alpha i}$ and the heating rate β is given by (1):

$$\ln \frac{\beta_{\rm i}}{T_{\alpha \rm i}^2} = -\frac{E_{\alpha}}{RT_{\alpha \rm i}} + \text{const.} \tag{1}$$



Fig. 6 The KAS lines for the copolymerization process of D-glucose monomer with styrene (Gm_S2)



Fig. 7 The KAS lines for the copolymerization process of D-glucose oligomer and HPMA (Go_HPMA1)

The subscript *i* denotes different heating rates. For each degree of conversion α , a corresponding $T_{\alpha i}$ and heating rate are used. Plot of $\ln(\beta i/T_{\alpha i}^2)$ against $1/T_{\alpha i}$ enables the calculation of E_{α} from the linear fits to experimental data [23]. The copolymerization process of the monomer and the oligomer derived from D-glucose into styrene and HPMA, respectively, was studied from the kinetics point of view using KAS method. Nine different conversions were considered and the activation energy of the process was evaluated as average of the nine values obtained for each conversion.

Figures 6 and 7 presents the KAS lines for the copolymerization process of Gm_S2 and Go_HPMA1; the KAS model is rather accurate for modeling this chemical process since the R^2 value is always above 0.9 for all the cases considered herein.

Tables 3 and 4 summarize all the values for the activation energies of the copolymerization processes calculated for all the mass ratios and conversions considered. It can be observed that the activation energy increases along

Table 3 The activation energies of the copolymerization processbetween the D-glucose monomer and styrene by KAS method

Conversion/%	$E_{\rm a}/{\rm kJ}~{\rm mol}^{-1}$					
	Gm_S1	Gm_S2	Gm_S3	Gm_S4		
10	79.436	98.188	80.689	86.049		
20	77.538	94.920	94.023	93.633		
30	74.834	93.840	102.411	103.875		
40	73.734	92.892	101.580	108.589		
50	72.895	92.992	102.95	111.341		
60	72.729	92.726	98.221	113.511		
70	73.202	92.601	101.888	114.201		
80	75.440	93.856	100.549	114.699		
90	81.927	97.132	98.479	114.317		
$E_{\rm a\ medium}/{\rm kJ\ mol^{-1}}$	75.75	94.35	97.86	106.69		

Table 4 The activation energies of the copolymerization process

 between the D-glucose oligomer and HPMA by KAS method

Conversion/%	$E_{\rm a}/{\rm kJ}~{\rm mol}^{-1}$				
	Go_ HPMA1	Go_ HPMA2	Go_ HPMA3	Go_ HPMA4	
10	55.57	76.65	123.48	114.26	
20	60.12	77.67	113.26	136.11	
30	59.34	75.91	104.41	142.80	
40	59.91	112.22	100	146.80	
50	58.65	132.86	98.03	147.98	
60	57.82	132.86	97.57	156.84	
70	57.99	147.06	94.57	161.30	
80	59.81	137.76	95.78	169.50	
90	60.94	117.43	95.28	152.57	
$E_{\rm a \ medium}/{\rm kJ} \ {\rm mol}^{-1}$	58.9	112.27	102.48	147.57	

the increase in styrene, respectively, in methacrylate mass ratio for both D-glucose monomer and D-glucose oligomer; the values corresponding to the copolymerization of the oligomer are slightly higher than those obtained for the monomer. The highest value of the activation energy is registered for the copolymerization process of Go with HPMA, in the greatest methacrylate content considered, while the lowest is again calculated for the same partners, but at the lowest methacrylate content. While for the oligomer copolymerization, the trend of the activation energy versus conversion is parabolic, with a maximum at a conversion of about 80 % in all the four mass ratios considered, the monomer copolymerization has the same parabolic behavior, but with a minimum registered at about 70 %.

The characterization of the copolymerized products using DMA

The mechanical properties of the glycopolymers were tested. The DMA allows us to evaluate three parameters which characterize a polymer: the storage modulus (E'), the loss modulus (E''), tan δ as function of temperature according to the strain frequencies [24, 25]. The peak of tan δ (defined as tan $\delta = E''/E'$) as function of temperature represents the glass transition temperature (T_g). The variation of the storage modulus E' and tan δ versus temperature for different strain frequencies is presented in Fig. 8 for Gm_S2 copolymers.

Table 5 presents the values for the storage modulus, the loss modulus and glass transition temperature for the glycopolymers derived from D-glucose monomer and styrene. Storage and loss modulus increase along the increase of the strain frequency; the biggest E' value, 2,020 MPa, is registered for Gm_S4 glycopolymer, at the highest frequency Fig. 8 DMA diagram for the Gm_S2 glycopolymers; storage modulus (E') and tan δ versus temperature



Table 5 The storage modulus (E'), the loss modulus (E''), the glass transition temperature (T_g) for the Gm_Sx glycopolymers

Sample	Frequencies/Hz	T/°C	T _g /°C				
		E'/MP	a	<i>E''</i> /MF	<i>E</i> "/MPa		
Gm_S1	1	329	60.8	757	77.3	94.2	
	2	345	60.4	958	77.6	78.3	
	5	338	52.6	1356	77.3	83.5	
	10	353	51.5	1461	77.1	84.1	
	20	369	50.5	1352	76.1	78.4	
Gm_S2	1	609	68.3	485	77.8	73.8	
	2	763	70.2	1199	93.9	83.0	
	5	1014	71.9	1133	97.4	91.5	
	10	1238	72.4	1445	84.4	86.2	
	20	1499	72.5	2002	83.5	71.3	
Gm_S3	1	730	66.9	626	77.2	91	
	2	818	68.6	906	79.7	89.8	
	5	1088	70.0	1561	81.4	88.6	
	10	1385	70.1	2263	81.4	78.2	
	20	1846	69.6	3174	80.5	78.7	
Gm_S4	1	1825	79.1	621	99.2	83.6	
	2	1866	80.1	637	101.9	85.8	
	5	1895	81.3	817	107.4	94.3	
	10	1933	82.8	1072	110.3	99.8	
	20	2020	85	1232	109.2	103.5	

(20 Hz) and 85 °C, while the lowest for Gm_S1 at 1 Hz and about 61 °C. Thus the strength of the glycopolymers increases with the increase in styrene content. This pattern is not found in the behavior of E'', which registers a maximum value for the Gm_S3 glycopolymer, at 80.5 °C

and 20 Hz, and a minimum for Gm_S2, at about 78 °C and 1 Hz. Glass transition temperature (considered the maximum of *tan* δ) has values above 0 °C and much higher than room temperature (71.3–103.5 °C) which explain the glassy nature of these polymers.

Table 6 The storage modulus (*E'*), loss modulus (*E''*) and glass temperature (T_g) values for Go_HPMAx glycopolymers

Sample	Frequency/Hz	<i>T</i> /°C				$T_{\rm g}/^{\circ}{\rm C}$
		E'/MP	a	<i>E"/</i> MI	Pa	
Go_HPMA1	1	659	40.5	640	45.2	39.4
	2	805	40.1	804	45.9	40.2
	5	1245	41.2	1206	46.2	41.8
	10	1349	41.5	1385	41.2	41.2
	20	1406	41.1	1596	43.2	42.0
Go_HPMA2	1	623	36.5	632	43.9	40.5
	2	785	36.1	796	43.6	41.0
	5	1102	36.4	1096	41.2	43.4
	10	1286	34.2	1249	45.1	42.8
	20	1358	33.8	1562	42.6	44.5
Go_HPMA3	1	604	32.1	625	44.9	42.7
	2	764	33.5	871	46.0	46.4
	5	998	33.8	1337	47.1	44.9
	10	1192	32.8	1746	46.4	53.2
	20	1305	31.9	2109	44.0	56.0
Go_HPMA4	1	580	30.1	604	42.0	45.8
	2	687	30.9	745	42.6	48.2
	5	895	31.2	896	41.9	47.9
	10	1063	30.0	1162	41.5	51.3
	20	1195	29.4	1384	40.9	52.4



Fig. 9 The TG lines for the D-glucose glycopolymers (Gm_Sx)

DMA analysis of the glycopolymers derived from D-glucose oligomer and HPMA reveals also a glassy nature of these materials, making them suitable, in practice for specific applications, mainly as glass replacements (due to their transparency), or as heat resistant materials (explained by the crosslinked structure). Table 6 reveals the variation of the storage and loss modulus, while showing the dependence of the glass transition temperatures with frequency and HPMA ratio; these glycopolymers show good stress resistance fact explained by their loss/storage modulus values that vary between 580 and almost 2,100 MPa [26, 27]. The biggest E' value is registered for the Go_HPMA1, at 41.1 °C and 20 Hz, while the lowest is shown by Go_HPMA4 at 1 Hz and 30.1 °C; which means that the most resistant to stress being the glycopolymer having the lowest HPMA content, in contrast with the situation shown by the Gm-derived glycopolymers. The trend for E'' is different, the biggest value being registered for Go_HPMA3, at 44 °C and 20 Hz, while the lowest loss

Fig. 10 The TG (thermogravimetric) curve and DTA (differential thermal analysis) curve for one D-glucose copolymer (Gm_S2)



Table 7 Mass loss for the styrene glycopolymers

Sample	Mass loss/%						
	20–100 °C	100–200 °C	200–300 °C	300–400 °C	400–500 °C		
Gm_S1	0.002	1.13	8.08	56.37	29.77		
Gm_S2	0.26	0.73	7.94	45.89	37.61		
Gm_S3	0.05	0.70	5.93	28.25	61.99		
Gm_S4	0.028	1.56	8.13	32.10	57.30		

 Table 8 Mass loss for the HPMA glycopolymers

Sample	Mass loss/%				
_	20–100 °C	100–200 °C	200–300 °C	300–400 °C	400–500 °C
Go_HPMA1	0.2	2.5	14.82	68.57	12.95
Go_HPMA2	0.15	3.7	14.28	67.01	14.76
Go_HPMA3	0.12	3.8	11.29	68.9	15.82
Go_HPMA4	0.1	3.5	12.39	74.08	9.28

modulus is 604, and corresponds to Go_HPMA4, at 1 Hz and 42 °C. The glass transition temperatures vary between about 40 and 56 °C, making these glycopolymers glassy and less heat resistant than the Gm-derived glycopolymers.

The characterization of the glycopolymers using TG

In order to determine the thermal stability of the copolymerized products, we performed thermogravimetrical analysis in nitrogen atmosphere and dynamic conditions with 10 °C min⁻¹ heating rate, at temperatures ranging between 20 and 500 °C. Figure 9 shows the TG diagrams for the Gm_Sx glycopolymers; this diagram let us to believe that the thermal decomposition of these glycopolymers occurs into two steps, each one probably

Fig. 11 The TG curves for the D-glucose glycopolymers (Go_HPMA)



corresponding mainly to the decomposition of the comonomers they were initially formed by. This fact is also proven by Fig. 10 that presents the superimposed TG and DTA (differential thermal analysis) diagrams of Gm_S2; we can clearly observe that the TG diagram shows two inflexions, corresponding to two DTA peaks at about 320 and 415 °C, respectively. We can thus appreciate that the first inflexion can be attributed mainly to the loss of some of the glycomonomer skeleton, while the second may be a result of the styrene residue degradation.

The glycopolymers analyzed have good thermal stabilities. The mass losses for the glycopolymers on different heating intervals are presented in Table 7. Up to 200 °C, the glycopolymers loose non-significant weight (less than 2 %) and up to 300 °C, they loose less than 9 %; so it can be concluded that they can be used in practice for different common applications that not require high temperature resilience. Heating up to 300 °C, the glycopolymers looses more than half of its mass (57 %); on the heating range of 400–500 °C glycopolymers losses most of the mass (62 %). Also, corroborated to the values of the glass transition temperatures we can conclude that up to 100 °C the glycopolymers suffer only phase transition modifications (melting especially), while at higher temperatures they begin to decompose.

The good thermal stability of the glycopolymers is also shown by Go-derived glycopolymers. Being also formed by copolymerization, the Go_HPMAx glycopolymers suffer similar decomposition process to Gm_Sx that occurs into two steps. Figure 11 shows the superimposed TG lines for the glycopolymers, while Table 8 presents their mass losses on different temperature ranges. Up to 200 °C, the glycopolymers loose non-significant mass (less than 4 %), and thus it can be stated that they can be used in practice for different common applications that not require high temperature resilience. On the other hand, the oligomer, as is, cannot be suited for common applications as a plastic materials, because heated up to 200 °C it looses almost one-fifth of its original mass [28]. That is the reason why these glycopolymers were obtained by the process of copolymerization, in order to obtain competitive plastic materials that can be applied in different fields.

Most of the mass is lost by the glycopolymers on the heating range of 300–400 °C, almost up to 75 %. As a thermal stability trend, we can conclude that the higher the percentage in HPMA, the more stable the glycopolymers become, but a smaller oligomer ratio sets the properties of these materials away from the class of glycopolymers and into the common aliphatic plastic materials category [29].

Conclusions

Two novel sugar-based monomer/oligomer were synthesized; the new monomer and oligomer were copolymerized using styrene and HPMA, respectively. DSC was performed in order to study the copolymerization process of the monomer and the oligomer into the chosen co-monomers, and the activation energy of this process was evaluated using KAS method; the values corresponding to the activation energy of the copolymerization process varied between almost 70 and 110 kJ mol⁻¹, for the monomer copolymerization and higher in the case of oligomer copolymerization because of its longer aliphatic skeleton (60 and 150 kJ mol⁻¹). The copolymers obtained were characterized via ATR-FTIR, this analysis proving that the copolymerization process that took place in bulk was complete, the specific signal for the double C=C bond being absent from the spectra. The TG study emphasized that the new plastic materials derived from the monomer and the oligomer have good thermal stabilities, and also that the process of thermal decomposition occurs in two steps as the DTA analysis revealed. DMA analysis of the glycopolymers concluded that these materials can be used in practice for different applications, due to their good storage/loss modulus values when exposed to different strain frequencies; also the storage modulus, the loss modulus for the same glycopolymer generally increase along the increase of the strain frequency, except for the T_g values which suffer rather random behavior.

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